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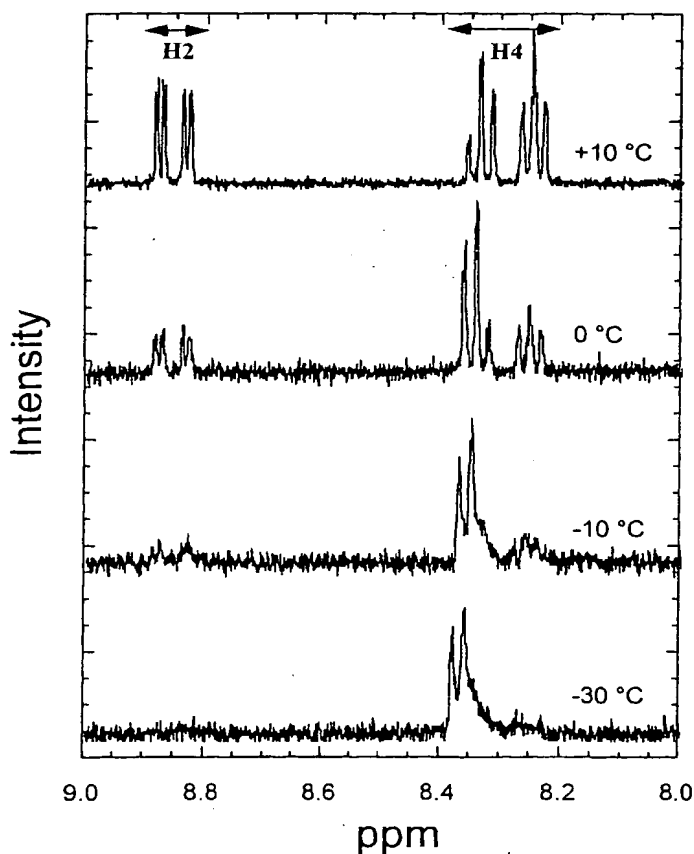
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[Continued on next page]

(54) Title: BLUE EMITTING TRIS (8-OXOQUINOLINE) ALUMINUM (III) (AlQ₃)



(57) Abstract: Process for the preparation of the facial isomer of tris(8-oxoquinoline)aluminum(III) (AlQ₃), comprising the step of heating α -AlQ₃ in solid phase at a temperature equal to or higher than 350°C but lower than 420°C, to obtain a mixture of γ -AlQ₃ and δ -AlQ₃.



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BLUE EMITTING TRIS (8-OXOQUINOLINE) ALUMINUM (III) (Alq₃)Technical field

The present invention relates to the isolation of the facial stereoisomer of the electroluminescent molecule tris(8-oxoquinoline)aluminum(III) (Alq₃), its mass
5 production and its characterization in solution and in the solid state.

Background art

The first highly efficient and low-voltage-driven organic electroluminescent devices (OLED), have been reported by Tang and Van Slyke (1), and were based on Alq₃. Fifteen years later, Alq₃ is still a key electroluminescent
10 compound, widely used in commercial devices and has become the prototype of a whole class of materials used as active layers in electroluminescent devices. Recently, significant improvements in device efficiency and stability have been obtained (2-6), and many efforts have been spent in order to extend and modify the typical green emission of Alq₃-based OLEDs, using
15 multilayers structures and chemical doping (7-9).

Tris-chelated octahedral complexes (such as Alq₃) can exist in the fac or mer isomeric forms. In the case of trisoxoquinoline complexes (Mq₃), only mer stereoisomers have been reported and characterized. The only reported example of a non-mer isomer is the Sbq₃ complex (10) which, however, is not
20 octahedral, thanks to the presence of a stereochemically active lone pair.

In the Alq₃ molecule, the possible existence of different geometrical isomers is still an unresolved issue. Despite of the many investigation efforts during several years (11-14), the facial stereoisomer of Alq₃ has never been directly observed. Invariably, spectroscopic studies on matrix-isolated molecules,
25 solutions and polymorphic crystal phases (13, 15) have evidenced the existence of the green-emitting mer isomer only. Curioni et al. have theoretically predicted through computational models (16) that the fac isomer is less stable ($\Delta E \approx 4$ kcal/mol) than the mer isomer and that it possesses a 0,3 eV higher energy gap (HOMO-LUMO), with a dipolar moment of 7 Debye (16).

30 Mer-Alq₃ crystallizes as α e β phases (and in a number of clathrates), whose

optical properties are determined by the nature of the π - π intramolecular contacts (15). In addition, partial crystallographic information on two phases, generated at elevated temperatures, called γ e δ , has been reported (15, 17).

Disclosure of the Invention

5 The main task of the present invention in the isolation of the facial isomer of Alq₃ (later shown to be a blue-emitting species) both in solution and in the solid state.

The aim of the present invention is to provide a procedure which allows to prepare large quantities of the blue-luminescent γ e δ phases, both
10 containing the elusive facial isomer of Alq₃.

Another aim of the present invention in to provide a method capable to stabilize the facial isomer of Alq₃ in solution.

One further aim of the present invention is to provide a method for obtaining blue-emitting thin films of Alq₃.

15 Another aim of the present invention is to provide blue-emitting electroluminescent devices based on Alq₃.

The above-mentioned aims and other aims which will become evident from the following descriptions have been reached through the solid-state synthesis of the facial isomer (γ -Alq₃) upon heating α -Alq₃ at temperatures
20 higher than 350°C, but lower than 420°C (typically 390 °C), followed by its transformation into the δ -Alq₃ phase by suspending the product obtained by heating in organic solvents (for example, acetone) and maintaining the suspension at room temperature.

Typically, heating of solid phase α -Alq₃ is performed with a
25 temperature gradient of 10°C/min in the 50 to 350°C temperature range.

Preferably, subsequent heating in the 350°C to 390-420°C range is performed with a temperature gradient of 1°C/min.

As a further aspect, the present invention offers a procedure for the preparation of thin films of δ e γ -Alq₃, which comprises the preliminary
30 preparation of δ e γ -Alq₃ solutions (for example, in CHCl₃) at temperatures

lower than -10°C , followed by the deposition of a thin layer of such solution on a substrate and followed by the fast solvent evaporation.

Solvent evaporation can also be accomplished at room temperature.

In the following, we report the direct observation of the fac isomer of the Alq_3 molecule by NMR spectroscopy as well as the key steps for its isolation and massive production, through a solid-solid reaction starting from the commercial (α - Alq_3) material. The optical emission properties of the fac isomer in solution, both in polycrystalline powders and films, are compared with those of the mer isomer. The crystal structure of the fac isomer in the γ and δ phases has been determined by X-ray powder diffraction methods (XRPD), which evidences the absence of π - π intermolecular contacts between oxyquinoline ligands.

The facial (fac) isomer shows a blue emission rather different from the green light emission typical for the meridional (mer) isomer.

A phase transformation diagram and a production method for the fac isomer is provided, starting from powders of the mer isomer.

The fac isomer crystallizes in two polymorphic species, the structures of which have been resolved by ab-initio X-ray powder diffraction methods. Both crystal phases show blue emission γ and δ - Alq_3 are the only known examples of Mq_3 species containing, in the solid state, the fac isomer.

The solution of the longstanding issue of the Alq_3 isomery opens the way to the development of blue-emitting electroluminescent devices based on Alq_3 .

Brief description of the drawings

The invention is described with more detail with the aid of the following figures:

figure 1: phase transformation diagram for Alq_3 ,

figure 2: ^1H NMR spectra (8-9 ppm range, at different temperatures) of δ - Alq_3 dissolved in CDCl_3 .

figure 3: top: photoluminescence spectra of fac and mer Alq_3 solutions, excited by an ultraviolet laser beam; bottom: photoluminescence spectra of α -

e γ -Alq₃ in the form of films, obtained from solutions and illuminated by a UV laser beam. The inserts show the molecular structures of the fac and mer isomers.

figure 4: crystal packing of the triclinic crystals of δ -Alq₃, viewed
5 down [001]. At this drawing resolution, the crystal structure of the trigonal γ -Alq₃ phase is rather similar.

Ways of carrying out the Invention

Alq₃ Isomery. Polycrystalline powders of α -Alq₃ are transformed predominantly into the γ phase upon heating at a temperature between 390°C
10 and 420°C at atmospheric pressure. We discovered that a few drops of liquid acetone favor the transformation of the γ phase into the δ phase, while seeding of supersaturated solutions of mer-Alq₃ with nuclei of γ (or δ) do not afford the δ phase. These experimental evidences have suggested the existence of a different Alq₃ isomer and prompted for new systematic spectroscopic and
15 structural analyses. The results of these investigations are reported in the phase transformation diagram depicted in figure 1, which shows the existence of four distinct solid phases for (unsolvated) Alq₃, based on the existence of two different stereoisomers. The fac isomer can only be obtained by a solid state reaction (blue arrow). However, diluted solutions of the fac isomer can
20 be obtained from the γ (or δ) phases at low temperatures, given that it is kinetically stable below -10°C.

At room temperature, independently from the starting material (α phase, γ phase or δ phase), solution ¹H and ¹³C-NMR experiments have shown that mer-Alq₃ is the only present species. However, upon suspending
25 solid γ - or δ -Alq₃ powders in CDCl₃ at a temperatures of -50°C, ¹H-NMR signals show the existence of only the fac-Alq₃ isomer. This neatly shows that γ - and δ -Alq₃ contain the fac isomer, which is kinetically stable, in the solid state, at room temperature.

From the spectra shown in figure 2 one can observe, at low temperatures,
30 the absence of the H2 signals near δ 8,8 ppm, which, coupled with the fact

that only the (magnetically equivalent) H4 nuclei are observed, shows that only the fac isomer is present. The increase of the signal-to-noise ratio observed upon heating the solution is a manifestation of the progressive transformation of the fac isomer into the more soluble mer-Alq₃.

5 Moreover, the spectra reported in figure 2 show that such isomerization begins at temperatures above ca. -10°C. It is worth noting that solutions prepared at room temperature from δ -Alq₃ only contain the mer isomer as a result of the rapid fac to mer transformation.

The photoluminescence spectra of solutions of mer- and fac-Alq₃ are
10 shown in figure 3 – top. The fac-Alq₃ solution has been prepared by dissolving powders of the γ or δ phases in CHCl₃ at -50°C. The photoluminescence of fac-Alq₃ in solution at -50°C is centered at 2,59 eV and has a brilliant blue color. The spectral position of the photoluminescence does not change at temperatures below -10°C, while at higher temperatures it
15 progressively shifts towards lower energies. It has been observed that the spectral emission maximum constantly decreases with increasing temperature, reaching a minimum value of 2,36 eV (green) at room temperature. This is in agreement with the NMR spectroscopic results, which show conversion of fac into mer at temperatures above -10°C. From the photoluminescence spectra,
20 we found that the transformation is complete after a few hours at room temperature.

Thus, the photoluminescence spectral emission features provides a characteristic fingerprint of each isomer.

Solid-solid Transformations. On the basis of ab-initio quantomechanical
25 computations, in the gas phase, the mer isomer is ca. 4 kcal/mol more stable than the fac isomer, but has significantly lower dipolar moment (4,1 vs. 7,1 Debye). If we assume that this also holds in solution, we can easily explain why the solution chemistry of Alq₃ is dominated by the mer isomer: in other words, one cannot obtain solutions of fac-Alq₃ through a chemical process in
30 solution. These results are fully in agreement with the long known ¹H-NMR

experiments, which revealed the mer isomer only at all investigated temperatures. (11). Upon increasing the temperature in the solid state, small energy differences can be overcome by entropic contributions, eventually assisted by cavity effects or a more efficient crystal packing. Indeed, the solid state transformation of mer into fac, starting from the α phase, occurs only near 390°C. Surprisingly, the γ phase, which is indefinitely stable in the solid state, can be easily transformed into the δ phase, at room temperature, if a few drops of liquid acetone are added. The acetone molecules give a limited mobility to the fac molecules which, well before isomerization, crystallize as the denser and more stable δ phase.

Crystal data for γ -Alq₃: C₂₇H₁₈AlN₃O₃, molar weight 409,43 g/mol, trigonal, space group P-3, $a=14.3807(6)$, $c=6.2107(4)$ Å; $V=1112.3(1)$ Å³, $Z=2$; $\rho_c=1.371$ g/cm³; R_{wp} and R_p : 0.133 and 0.102 for 3501 data collected in the $5<2\theta<75^\circ$ range. R_{Bragg} 0.037.

Crystal data for δ -Alq₃: C₂₇H₁₈AlN₃O₃, molar weight 409,43 g/mol, triclinic, space group P-1, $a=14.44479(9)$, $b=13.2620(7)$; $c=6.1887(4)$ Å; $\alpha=95.865(5)$; $\beta=88.613(5)$; $\gamma=113.922(4)^\circ$; $V=1078.1(1)$ Å³, $Z=2$; $\rho_c=1.415$ g/cm³; R_{wp} and R_p : 0.161 and 0.124 for 3501 data collected in the $5<2\theta<75^\circ$ range. R_{Bragg} 0.061.

Crystals of γ -Alq₃ belong to the trigonal space group P-3. Fac-Alq₃ shows C₃ symmetry. δ -Alq₃ is triclinic, space group P-1, thus its three oxoquinoline ligands are crystallographically independent. Figure 4 shows the pseudo-trigonal crystal packing of δ -Alq₃. The crystal structure of γ -Alq₃ is similar, with the molecules lying on threefold crystallographic axes of the trigonal space group P-3. The two phases are correlated by a proper group-subgroup relationship, since the δ phase can simply be obtained by removing the threefold axes of the γ phase, but maintaining all inversion centers. The small differences in the crystal packings of γ - and δ -Alq₃ are evident in their Raman spectra, which contain the same intramolecular phonon modes, but different lattice modes (20). The optical emission spectra of γ - and δ -Alq₃ are identical,

as later discussed.

α -Alq₃ (15), γ - and δ -Alq₃ possess similar lattice parameters, thus showing that different stereoisomers can adopt similar packing modes. The common motif is the presence of chiral columns of [Alq₃]_∞, parallel to the c axis, pseudotrigonally packed in the ab plane. In all these phases, thanks to their centrosymmetric nature, molecules of (\pm)Alq₃ and the columns of opposite chirality coexist in an equimolar ratio.

Solid state optical properties. The possibility of preparing stable blue emitting thin films of Alq₃ derives from the comprehension of the Alq₃ isomery and from the phase transformation diagram. The availability of stable solutions of fac-Alq₃ allows the preparation of films which maintain the characteristic blue emission of the fac-Alq₃ isomer. Figure 3 – bottom – shows films obtained by deposition of a solution of fac-Alq₃ and of a solution of mer-Alq₃ on quartz substrates. At low temperatures, the fac to mer transformation is relatively slow and allows the stabilization of the fac isomer in the solid phase after solvent evaporation, even when the substrate is kept at room temperature. Figure 3 – bottom – shows the photoluminescence spectra measured on polycrystalline powders of α -Alq₃ (green) and δ and γ -Alq₃ (blue) at 4K. As mentioned above, there is no significant difference between the photoluminescence spectra of the γ and δ phases. The spectra of α - and γ -Alq₃ clearly show the same vibronic progression due to the bending mode at 525 cm⁻¹ (21) which, in both cases, is described by a Huang-Rhys factor of ca. 2,6. This indicates that in both isomers the same strong electron-phonon coupling is present in the radiative electronic transition.

The photoluminescence spectra of the thin films of the mer and fac isomer are similar to those of the powders of α and γ (or δ) but are red-shifted and, even at low temperatures, do not show the vibronic progression. This behavior is typical in thin films of Alq₃ and has been interpreted in the past as a consequence of the coexistence of the two isomers (2, 16). In the light of the results here reported, the amorphous nature of the thin films of Alq₃ is more

likely attributed to the polymorphism, rather to the racemic nature, of Alq₃.

The discovery of blue emitting stable phases of Alq₃ allows the fabrication of blue emitting efficient OLEDs based on Alq₃. This, together with a deeper knowledge of the optical and electronic properties of Alq₃, may
5 allow the use of a unique active material in color visualization devices of the RGB (red, green, blue) type.

NMR Spectroscopy: α -Alq₃ can easily be dissolved in a number of organic solvents; differently, δ -Alq₃ shows much lower solubility. In a first series of NMR experiments, powders of α -Alq₃ and δ -Alq₃ were dissolved in
10 CDCl₃ at room temperature. The ¹H and ¹³C NMR spectra have been collected on a 400 MHz Bruker NMR AVANCE instrument.

The room temperature ¹H-NMR spectrum of mer-Alq₃ fully agrees with that reported in (18). The molecular aggregation in solution, originally observed through fluorescence spectroscopy (15) has been confirmed from
15 the concentration dependent chemical shifts of the "external" protons, particularly of H4. A peculiarity of this spectrum is the anomalous lowering (1,5 ppm) of the chemical shift of one of the three H2 atoms. This is due to the unique intramolecular environment of this H2 atom, pointing toward an adjacent aromatic ring. This information is of high relevance in the
20 interpretation of the ¹H NMR spectrum of the fac-Alq₃ isomer at -50°C. Indeed, the stereochemistry of fac-Alq₃ requires that all H2 atoms feel diamagnetic ring currents.

In a second series of NMR experiments, solid δ -Alq₃ has been cooled to liquid nitrogen temperature in an NMR tube. CDCl₃ has been added and the
25 temperature has been raised to -50°C at controlled rate in about 30 minute time. A series of ¹H NMR spectra has been measured at this temperature, which demonstrated the absence of molecular isomerisation even after a few hours. Further spectra were subsequently collected upon increasing the temperature by 10° intervals, up to room temperature. 10 minutes delays have
30 been given after each spectrum, in order to thermally stabilize the system.

The fac-Alq₃ isomer shows a simpler ¹H NMR spectrum, due to its C₃ symmetry. It consists of two multiplets centered near δ 8,36 ppm (H4) and δ 7,52 ppm (H6) and of many severely overlapped peaks, in the 7,1 to 7,4 ppm range (H2, H3, H5 e H7). All resonances of the H2 atoms are shifted to high fields, just as the unique H2 atom of mer-Alq₃ (δ 7,22 ppm, see (18)).

Powder X-ray diffraction analysis: indexing of the diffraction pattern of γ-Alq₃ confirmed the reported trigonal metrics and gives better figures of merit [*a* = 14.364, *c* = 6.208 Å; *M*(22) = 42, *F*(22) = 56 (0,009, 43)]. On the basis of a complete Rietveld analysis, the correct trigonal space group is not P-31c (15) but P-3 (00l reflections being obscured by accidental overlap). We note the original assignment of γ-Alq₃ as based on the mer isomer was tentatively presented using a low quality XRPD pattern (not allowing a complete modeling by the Rietveld technique), together with the consideration that in the sublimed powders only mer-Alq₃ was present. The complete Rietveld analysis here reported determines in a definitive manner the molecular (fac) and crystal line structure of γ-Alq₃. Indexing of the diffraction pattern of the δ polymorph leads to a triclinic cell [*a* = 14.503, *b* = 13.288, *c* = 6.208 Å; α = 95,9; β = 89,7; γ = 114,0; *M*(23) = 21, *F*(23) = 53 (0,009, 47)]. The structure resolution of γ- and δ-Alq₃ has been performed by the simulated annealing technique (Bruker AXS 2000; Topas V2.0.). The final refinement of the structural models of biphasic mixtures have been performed on two different sets of data (Γ and Δ, rich, respectively, in γ- and δ-Alq₃,) collected in the 5<2θ<75° range, with step size Δ2θ = 0,02°, *t* = 60 (Γ) or 100 (Δ) s step⁻¹. Both in the solution and in the refinement steps we used oxyquinoline fragments of ideal geometry, hinged about the Al atom through flexible restraints [on the intramolecular contacts 1,2 Al/X and 1,3 X/X (X = N,O) of a fac stereoisomer]. The XRPD traces have been collected on a conventional powder diffractometer (Philips PW1820) equipped with Soller slits, a secondary beam graphite monochromator, and Cu-Kα radiation, λ = 1.5418 Å, 40 KV, 40 mA.

The following examples are given for illustration but not limitation of the present invention.

Examples

Example # 1

5 **Preparation of γ -Alq₃ (polycrystalline powders):** commercial α -Alq₃ is heated to 395°C using a temperature gradient of 10°C/minute in the 50-350°C range and of 1°C/minute between 350°C and 395°C. After maintaining the system at this temperature for some minutes, is its rapidly cooled down to room temperature. The XRPD analysis show that the resulting powders, of
10 dark yellow color, consist of a mixture of the γ -Alq₃ and δ -Alq₃ phases. On using 15 mg of α -Alq₃ powders, the γ -Alq₃/ δ -Alq₃ ratio is close to 10/1; such ration is not significantly modified by an increase of the heating rate up to 10°C/minute or by a decrease of the cooling rate, down to 1°C/minute. Moreover, this ratio remains unchanged by heating at the maximum pre-
15 sublimation temperature of 410°C. The use of larger amounts of the starting material (grams), however, was found to typically afford lower γ -Alq₃/ δ -Alq₃ ratios.

Example # 2

20 **Preparation of δ -Alq₃ (polycrystalline powders):** γ -Alq₃, prepared as described in the Example # 1 and thus containing already small quantities of δ -Alq₃, is suspended in acetone for 15 hours at room temperature with occasional stirring. Through centrifugation, the resulting light yellow powder is then recovered. The XRPD analysis shows the presence of (almost pure) δ -Alq₃ phase, accompanied by less than 4% residual γ -Alq₃. Neither the
25 solvent volume nor the γ -Alq₃/ δ -Alq₃ ratio in the starting powders have any influence on the γ -Alq₃/ δ -Alq₃ ratio in the final mixture.

The disclosures in Italian Patent Application No. MI2002A001330 from which this application claims priority are incorporated herein by reference.

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CLAIMS

1. Process for the preparation of the facial isomer of tris(8-oxoquinoline)aluminum(III) (Alq_3), comprising the step of heating $\alpha\text{-Alq}_3$ in solid phase at a temperature equal to or higher than 350°C but lower than
5 420°C , to obtain a mixture of $\gamma\text{-Alq}_3$ and $\delta\text{-Alq}_3$.

2. The process according to claim 1, further comprising a step of suspending said mixture in an organic solvent and keeping said suspension at ambient temperature.

3. The process according to claim 2, wherein said organic solvent is
10 acetone.

4. Process for obtaining a thin film of the facial Alq_3 , comprising the steps of preparation of a solution of facial Alq_3 in a solvent, at a temperature lower than -10°C , application of a thin layer of such solution onto a substrate, and evaporation of the solvent to obtain a thin film.

15 5. The process according to claim 3, wherein said solvent is CHCl_3 .

6. Process for obtaining a thin film of facial Alq_3 , comprising the step of heating a thin film of meridional Alq_3 at a temperature in the range from 390 to 420°C .

7. Blue emitting electroluminescent device based on facial Alq_3 .

20 8. Use of facial Alq_3 for making electroactive devices suitable for charge transport and/or recombination and/or for light emission.

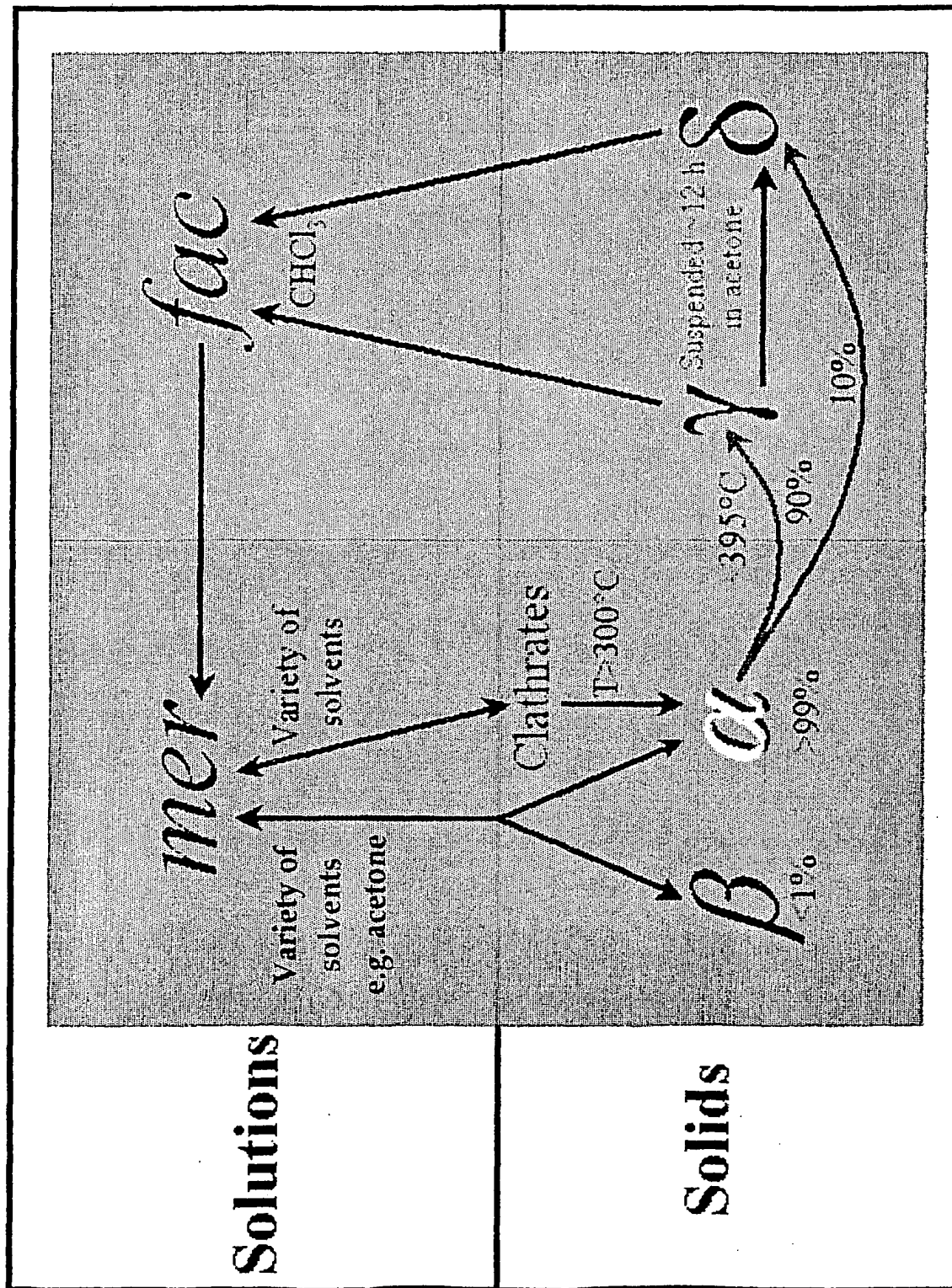


Fig.1

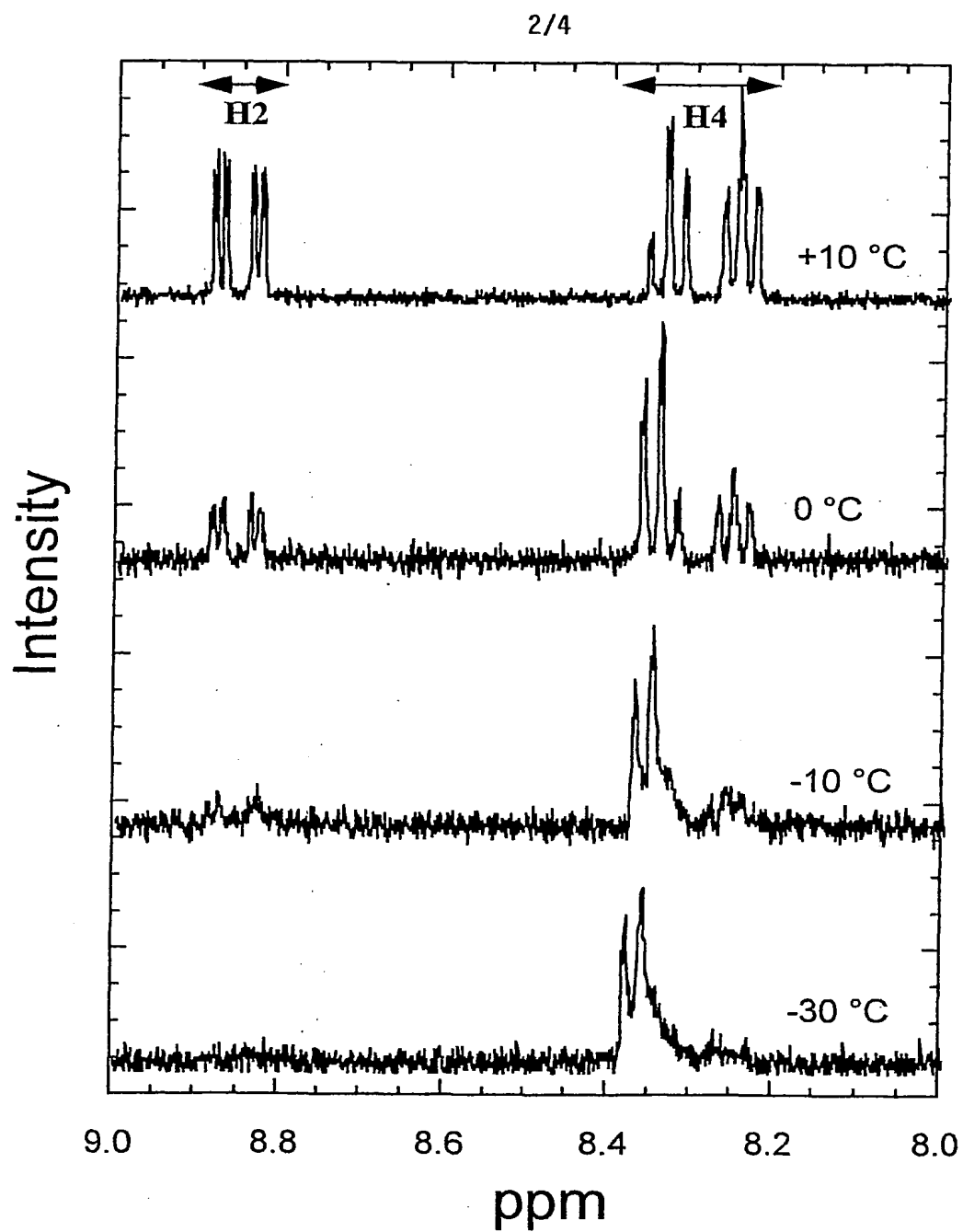


Fig.2

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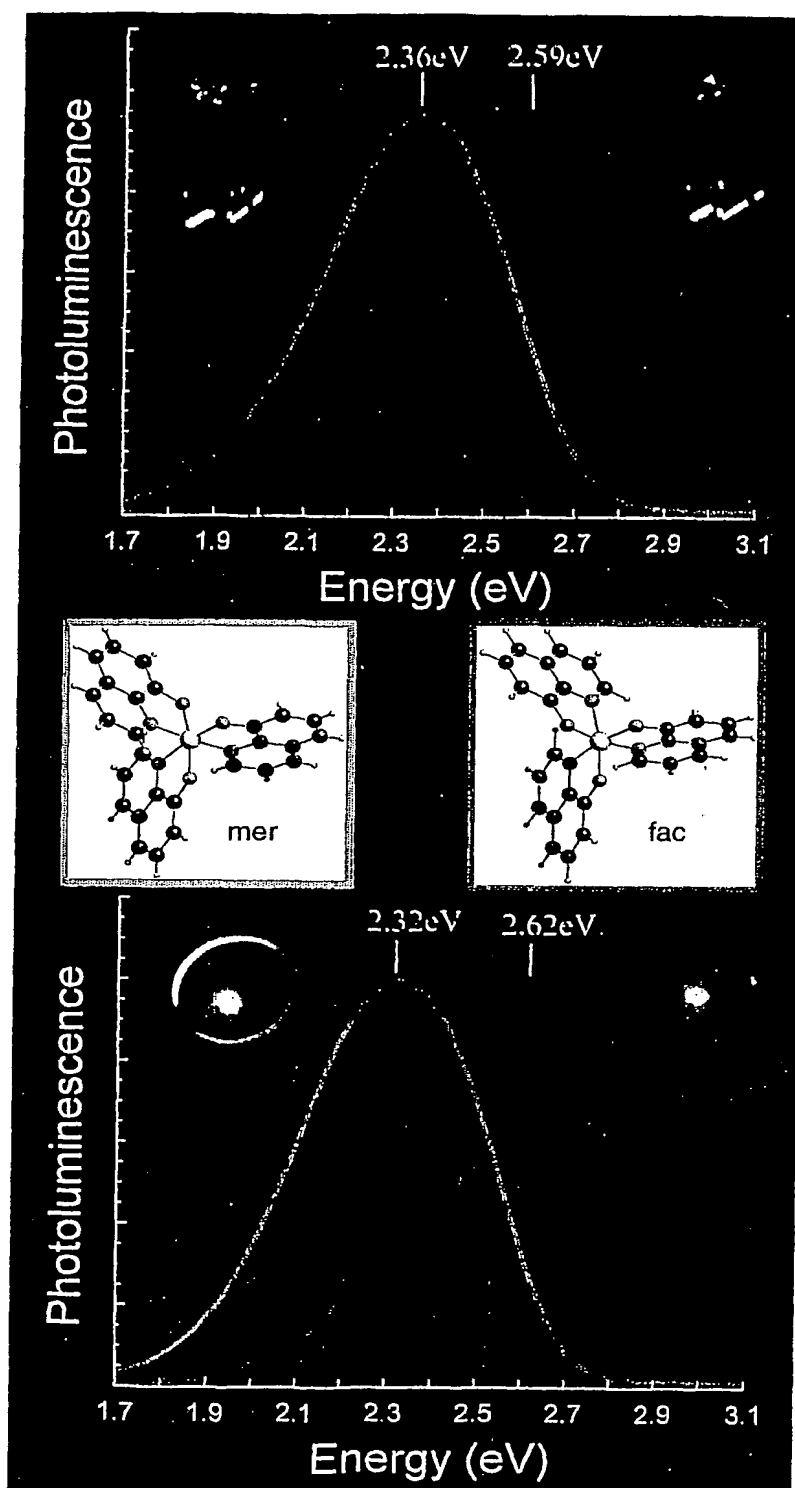
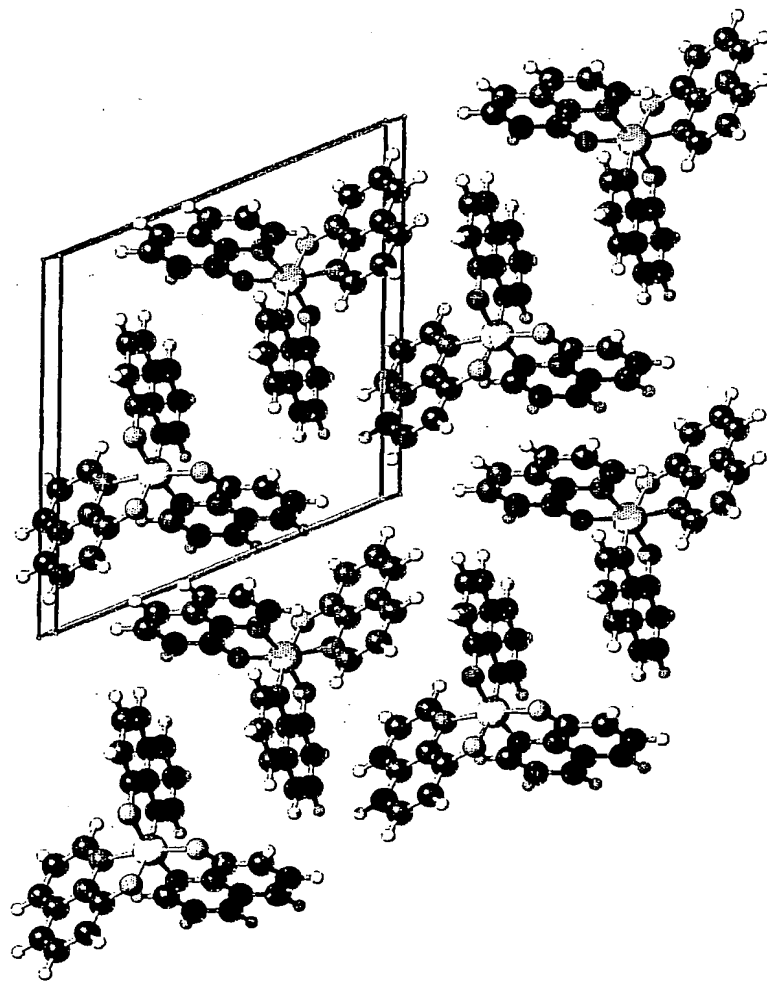


Fig. 3

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Fig. 4



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06197

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D215/30 C09K11/06 H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D C09K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 117, no. 16, 19 October 1992 (1992-10-19) Columbus, Ohio, US; abstract no. 160319, MORI, YASUSHI ET AL: "Organic electroluminescent diode element" XP002254143 abstract & JP 04 085388 A (TOSHIBA K. K., JAPAN) 18 March 1992 (1992-03-18) --- -/--	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

11 September 2003

Date of mailing of the international search report

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP. 03/06197

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